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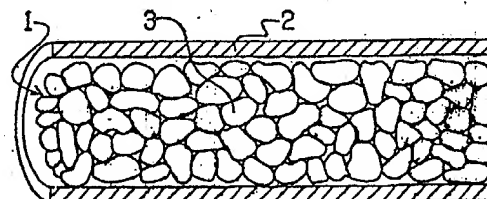
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54 Process for manufacturing a compound oxide-type superconducting wire.

57 A process for manufacturing a wire made of oxide which is applicable for manufacturing a superconducting coil or the like. The process includes steps comprising preparing a mass of oxide having superconductivity from powder material, covering the mass of oxide with a metal pipe, and then reducing the diameter of the metal pipe containing the mass of oxide therein into a wire form by such plastic deformation that exert mainly compressive strain upon the metal pipe. The mass of oxide may be a compound oxide having Perovskite-type crystal structure exhibiting superconductivity. The metal pipe may be made of a metal selected from a group comprising Cu, Al, Nb, V, Mo, Ta, and Ag and of an alloy including these metals as the base. The mass of oxide may be produced by steps including extruding a powder material into a rod shape and then sintering the molded rod at a temperature ranging from 700 to 1,000 °C. The plastic deformation of the metal pipe containing the mass of oxide therein may be carried out by swaging.

FIGURE 1



Description

PROCESS FOR MANUFACTURING A COMPOUND OXIDE-TYPE SUPERCONDUCTING WIRE

Background of the invention

Field of the invention

The present invention relates to a process for manufacturing a superconducting wire of compound oxide-type ceramic which can be used for a superconducting coil or the like.

Particularly, the present invention relates to a process for manufacturing a superconducting wire made of sintered ceramic of compound oxide having higher critical current density and higher critical transition temperature of superconductivity.

Description of the related art

The superconductivity is a phenomenon in which the electrical resistance become zero and hence can be utilized to realize power cables and a variety of devices and apparatus which are requested to reduce consumption of electrical energy and several ideas of its applications which utilize the phenomenon of superconductivity have been proposed.

In fact, the superconductivity are applicable in a variety of industrial fields, for example in the field of electrical power supply such as fusion power, MHD power generation, power transmission, or electric power reservation; in the field of transportation such as magnetic levitation trains, magnetically propelling ships; in the medical field such as high-energy beam radiation unit; in the field of science such as NMR or high-energy physics; or in the field of sensors or detectors for sensing very weak magnetic field, microwave, radiant ray or the like as well as in the field of electronics such as Josephson Junction devices and high-speed computers with reduced energy consumption.

However, their actual usage have been restricted because the phenomenon of superconductivity can be observed only at very low cryogenic temperatures. Among known superconducting materials, a group of materials having so-called A-15 structure show rather higher T_c (critical temperature of superconductivity) than others, but even the top record of T_c in the case of Nb_3Ge which showed the highest T_c could not exceed 23.2 K at most.

This means that liquidized helium (boiling point of 4.2 K) is only one cryogen that can realize such very low temperature of T_c . However, helium is not only a limited costly resource but also requires a large-scaled system for liquefaction. Therefore, it had been desired to find another superconducting materials having much higher T_c . But no material which exceeded the abovementioned T_c had been found for all studies for the past ten years.

It is known that certain ceramics material of compound oxides exhibit the property of superconductivity. For example, U. S. patent No. 3,932,315 discloses Ba-Pb-Bi-type compound oxide which shows superconductivity. This type superconductor, however, possess a rather low transition temperature of lower than 13 K and hence usage of liquidized

helium (boiling point of 4.2 K) as cryogen is indispensable to realize superconductivity.

Possibility of existence of a new type of superconducting materials having much higher T_c was revealed by Bednorz and Muller who discovered a new oxide type superconductor in 1986 (Z. Phys. B64 (1986) p189)

This new oxide type superconducting material is $[La, Ba]_2CuO_4$ which is so-called the K_2NiF_4 -type oxide having such a crystal structure that is similar to Perovskite-type superconducting oxides which were known in the past (for example, $Ba_{1-x}Bi_xO_3$ disclosed in U.S. Patent No. 3,932,315). The K_2NiF_4 -type oxides show such higher T_c as about 30 K which is extremely higher than that of known superconducting materials.

As the compound oxide type superconductors consisting of oxides of elements of IIa and IIIa groups in the Periodic Table, it can be mentioned those of, so to say, quasi-Perovskite structure which can be considered to have such a crystal structure that is similar to Perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite such as $Ba_2YCu_3O_{7-\delta}$ in addition to the abovementioned K_2NiF_4 -type oxide such as $[La, Ba]_2CuO_4$ or $[La, Sr]_2CuO_4$. Since these superconducting materials show very high T_c of 30 to 90 K, it becomes possible to use liquidized hydrogen (b.p. = 20.4 K) or liquidized neon (b.p. = 27.3 K) as a cryogen for realizing the superconductivity in practice. Particularly, hydrogen is an inexhaustable resource except for danger of explosion.

Therefore, the application of these superconducting oxide having the layered perovskite structure in the field of electric power transmission have become the object of public attention. However, their molding have been limited to powder sintering technique, so that they are molded into a desired shape by means of a combination of press-molding and sintering or so-called HIP (hot isostatic pressing). Thus, the above mentioned new type superconducting materials which was just born have been studied and developed only in a form of sintered bodies as a bulk produced from powders. In other words, no attempt have been tried to use the oxide as a medium for transmitting electric power and no trial to shape the oxide into a wire form have not been made except very rare case.

The oxide type ceramic materials possess no superior plasticity or processability in comparison with well-known metal type superconducting materials such as Ni-Ti alloy, and therefore they can not or are difficult to be shaped or deformed into a wire form by conventional technique such as wire-drawing technique in which superconducting metal is drawn directly or in embedded condition in copper to a wire form.

It is proposed in Japanese patent laid-open No. 61-131,307 a method for manufacturing a superconducting wire from a metal type supercon-

ducting material which is apt to be oxidized and very fragile such as $\text{PbMo}_{0.35}\text{Ss}$, comprising charging the material powder in a metal shell, extruding the metal shell filled with the material powder at higher than $1,000^\circ\text{C}$, and then drawing the extruded composite. This metal working technique, however, can not apply directly to ceramic material consisting of compound oxide, because the compound oxide type superconducting materials can not exhibit the superconductivity if not the specified or predetermined crystal structure is realized. In other words, a superconducting wire having higher critical temperature and higher critical current density and which is useable in actual applications can not be obtained outside predetermined optimum conditions. In particular, if not the shell is selected from proper materials, the resulting compound oxide will be reduced due to chemical reaction with the metal of the shell, resulting in poor or inferior properties of superconductivity.

In the field of ceramic molding, it has been the general practice for manufacturing an elongated article such as wires or rods to add an organic binder to the material powder of ceramic in order to facilitate shaping or molding of the powder material. Thus, a mixture of the powder material and the organic binder is shaped into a rod by means of an extruder or a press machine and then the shaped rod is passed directly or through a trimming or cutting stage to an intermediate sintering stage to remove the organic binder before it is fed to the final sintering stage.

The combination of the abovementioned press-molding and trimming or cutting operations lose much material of expensive ceramics, so that not only economy of material is low but also a dimensional ratio of longitudinal direction to cross sectional direction of the rod can not be increased. Therefore, this process can not be used in practice.

The extrusion technique is much better than the press-molding technique in the economy of material and productivity, but requires great quantities of organic binder added to the powder material. This organic binder is difficult to be removed completely during the intermediate sintering stage and hence remain in the finally sintered article, resulting in a cause of defects of the product which will lower the strength and the resistance to flexion. Therefore, it is difficult to manufacture a fine rod of ceramics having higher dimensional ratios of longitudinal direction to cross sectional direction according to the extrusion technique.

In order to realize a reliable and practical superconducting structure, it is indispensable that the structure possesses enough strength and tenacity which is sufficient to endure bending force during usage and also has a finer cross sectional dimension as possible in such manner that it can transmit currency at higher critical current density and at higher critical temperature.

The present applicant, in the previous U. S. patent application No. titled "process for manufacturing a superconducting wire of compound oxide-type ceramic" filed on February 5, 1988, a method for manufacturing a superconducting elongated article

including steps comprising filling a metal pipe with material powder of ceramic consisting of compound oxide having superconductivity, performing plastic deformation of the metal pipe filled with the ceramic metal powder to reduce the cross section of the metal pipe, and then subjecting the deformed metal pipe to heat-treatment to sinter the ceramic material powder filled in the metal pipe.

This previous method itself is satisfactory, but requires the first step of compacting material ceramic powder in a metal pipe, so that a skilled hand is required to obtain the high compacting density. If the powder is not filled in desired compacted condition, higher critical current density (J_c) can not be expected. We continued to develop another technique which can support superconducting material in an outer metal layer and finally found out the present invention.

Therefore, an object of the present invention is to provide a process for shaping the abovementioned oxide into a wire form so that an oxide wire can be manufactured without difficulty.

Another object of the present invention is to provide a process for manufacturing a fine superconducting wire of compound oxide type sintered ceramic having higher critical current density and higher critical temperature.

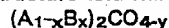
Summary of the Invention

A subject of the present invention resides in a process for manufacturing a wire made of oxide characterized by steps comprising preparing a mass of oxide having superconductivity from powder material, covering the mass of oxide with a metal pipe, and then reducing the diameter of the metal pipe containing the mass of oxide therein into a wire form by means of plastic deformation which is performed under compressive strain.

The term of "mass of oxide having superconductivity" means a self-supporting body or block being made of oxide and having superconductivity by itself. In general, this mass of oxide may be a preliminary sintered body or a solid solution obtained from material powder mixture and can be produced by molding a powder mixture into a rod shape and then heating the molded rod to produce a mass of oxide having superconductivity.

Description of the Preferred Embodiments

The mass of oxide having superconductivity which can be used in the process of the present invention may be made of an oxide having a layered perovskite structure and having the general formula:



In which "A" stands for at least one element selected from lanthanide elements of the Periodic Table, "B" stands for at least one element selected from a group comprising Ia, IIa and IIIa elements of the Periodic Table, "C" stands for at least one element selected from a group comprising Ib, IIB, IIIB elements or transition elements of the Periodic, and small letters "x" and "y" are numbers which satisfy $0 < x < 1$, and $0 \leq y < 4$.

As the element of Ia group in the Periodic Table, it can be mentioned H, Li, Na, K, Rb, Cs and Fr. The

elements of IIa in the Periodic Table may be Be, Mg, Ca, Sr, Ba and Ra. The elements of IIIa in the Periodic Table may be Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, Mo and Lr. The elements of Ib in the Periodic Table may be Cu, Ag and Au. The elements of IIb in the Periodic Table may be Zn, Cd and Hg. The elements of IIIb in the Periodic Table may be B, Al, Ga, In and Tl.

Among a variety of mass of oxide having superconductivity which can be used in the present invention, it can be mentioned following examples:

-a mass of compound oxide containing at least one element selected from IIa groups of the Periodic Table, at least one element selected from IIIa groups of the Periodic Table, and copper, for example, La-Sr-Cu-O type ceramics and La-Ba-Cu-O type ceramics, more precisely, compound oxides having the crystal structure of K_2NiF_4 -type oxides, such as $[La, Ba]_2CuO_4$ or $[La, Sr]_2CuO_4$; Y-Ba-Cu-O type ceramics, Y-Sr-Cu-O type ceramics, more precisely, compound oxide having layered perovskite or oxygen deficient perovskite structure, such as $YBa_2Cu_3O_{7-x}$ or $YSr_2Cu_3O_{7-x}$ ("x" stands for a number satisfying $0 < x \leq 1$); and more generally, Ln-(Ba,Sr)-Cu-O type ceramics (wherein, "Ln" stands for lanthanide element) of compound oxide such as $HoBa_2Cu_3O_{7-x}$, $HoSr_2Cu_3O_{7-x}$ ("x" stands for a number satisfying $0 < x \leq 1$);

-a mass of compound oxide containing at least two elements selected from IIa groups of the Periodic Table, for example Ca and Sr, at least one element selected from IV and V groups of the Periodic Table, such as Bi, and copper, but containing no IIIa groups element of the Periodic Table, for example, Ca-Sr-Bi-Cu-O type ceramics such as $CaSrBiCu_2O_{7-x}$ ("x" stands for a number satisfying $0 < x \leq 3$); and

-a mass of compound oxide composed mainly of the abovementioned elements and a small amount of additives selected from a group comprising IVb, Vb, VIb and VIIIb groups of the Periodic Table, such as Ti.

The mass of oxide used in the present invention are not limited to those abovementioned.

The mass of oxides may be produced by a combination of molding and sintering. For example, the mass of oxide can be produced by steps comprising mixing material powders which may be oxides, carbonates, nitrate, sulfates or other compound of the constituent elements of the compound oxide, for example, a powder mixture of Y_2O_3 , $BaO_2(SrO_2)$ and CuO , in such manner that atom ratios of Y:Ba(Sr):Cu in the mixture correspond to the final atom ratios of 1:2:3 which is realized in the product of superconducting wire, shaping or molding the mixture by means of an extruder, a press or the like, and then sintering the shaped powder mixture in an oxygen containing atmosphere.

In the case of Ca-Sr-Bi-Cu-O type ceramic, the atom ratios of Ca:Sr:Bi:Cu may be adjusted to 1:1:1:2 by utilizing a powder mixture of Bi_2O_3 , $SrCO_3$, $CaCO_3$ and CuO .

The shaping or molding of the powder mixture can be carried out by any one of known powder molding techniques, such as extrusion, compression, hot-

pressing or the like. In a preferred embodiment of the present invention, the molding is performed by means of a friction driving type extruder.

The sintering may be carried out at a temperature range of from 700 to 1,000 °C which is selected in the function of the constituent elements of the ceramics. Therefore, the resulting sintered articles possess as a whole the crystal structure which exhibits superconductivity and hence there remain no portion where superconductivity is not exhibited.

The metal pipe may be made of any metal which can endure the plastic deformation used in the present invention, and may be selected from a group comprising Cu, Al, Nb, V, Mo, Ta, and Ag and of an alloy including these metals as the base. These metal pipe made of ordinary conductor function as a stabilizer for a superconducting wire, namely the metal pipe will become a electric current circuit when superconductivity break accidentally. In other words, the method of the present invention permit to produce a protective layer simultaneously when a superconducting wire is manufactured.

The plastic deformation may be performed mainly under compressive condition, for example by means of swaging unit or rolls. It is important not to exert excess traction to the composite pipe of the metal pipe and the mass of oxide. In other words, it is necessary to carry out deformation of the composite mainly under compressed condition rather than under force of traction or drawing. The reason is that the mass of oxide used in the present invention have a layered perovskite structure, so that sliding among layers along c-axis occur under the compressive force, which permit a small amount of plastic deformation of the mass of oxide. Thus, the plastic deformation performed mainly under compression strain according to the present invention permit to perform such wire-manufacturing operation that can maintain continuity of the mass of oxide. To the contrary, it is difficult to produce a wire having sufficient continuity of the mass of oxide by a conventional wire-drawing in which plastic deformation is effected mainly by traction force. The abovementioned continuity of the mass of oxide can be assured also by the presence of the outer metal pipe which surrounds the inner mass of oxide.

It is also known that the abovementioned compound oxide show anisotropy of electric current so that the the superconducting current flow much easily in parallel with c-axis of crystals of the abovementioned compound oxide. Therefore, a higher amount of electric current, and hence higher critical current density (J_c) can be obtained according to the present invention, since sliding among crystal layers is effected along the c-axis and hence c-axis of the mass of oxide become in parallel with an axial direction of the resulting superconduction wire.

In conclusion, the process of the present invention can increase the critical current density (J_c) by increment of compacting density due to plastic deformation performed mainly compression force and by improvement of orientation of c-axis.

It is also preferable to re-heat the mass of oxide after the plastic deformation complete in order to

improve the superconducting condition of the resulting superconducting wire. This heat-treatment may be carried out at a temperature ranging from 700 to 1,100 °C. It is also possible to remove the outer metal pipe mechanically or chemically after the plastic deformation.

Now, an apparatus which can be used to realize the abovementioned process according to the present invention will be described with reference to attached drawings which are not limitative of the present invention.

Brief description of the drawings

Fig. 1 illustrates a cross sectional view of a metal pipe containing a mass of oxide therein from which a superconducting wire is produced according to the present invention.

Fig. 2 illustrates a cross sectional view which shows a condition of the metal pipe after it is subjected to plastic deformation.

Fig. 3 shows the principle of a friction driving type extruder in a cross sectional view, which is used in one embodiment of the present invention.

Fig. 4 illustrates a perspective view of swaging die set which is used in the preferred embodiment of the present invention.

Referring to Fig. 1 and Fig. 2 which illustrate two different conditions of mass of oxide 1 contained in a metal pipe 2 before and after it is subjected to plastic deformation according to the present invention. In Fig. 1, a mass of oxide 1 which has been produced by an extruder shown in Fig. 3 is covered with a metal pipe 2.

Fig. 3 illustrates a friction driving type extruder which may be used for producing the mass of oxide 1. This friction driving type extruder itself is well-known and is described in Japanese patent laid-open NO. 47-31859. In this type extruder, material powder 4 is fed by screw feeder (not shown) into an annular groove (not shown) defined between a stationary member 6 (so-called as a shoe) and a rotary member (so called as a wheel), so that the material powder 4 is driven or entrained by the wheel 5 and finally extruded through an orifice 7 in a form of a fine rod.

The resulting rod is then heated in an oven (not shown) at about 700 to 1,100 °C to produce a sintered mass of oxide 1.

After the mass of oxide is covered with a metal pipe 2 (Fig. 1), the composite of the metal pipe 2 and the mass of oxide 1 is subjected to plastic deformation to reduce its diameter to the final dimension (Fig. 2).

This plastic deformation may be performed by swaging operation illustrated in Fig. 4. Fig. 4 shows a die assembly for performing swaging by means of four swaging dies 8 each of which reciprocates along a radial direction, so that the composite pipe (1,2) is compressed under compressive force while is advanced at a very low speed to obtain a wire comprising a reduced metal pipe 2' and a reduced mass of oxide 1'.

Now, the process according to the present invention will be described with reference to illustra-

tive Examples, but the scope of the present invention should not be limited thereto.

Example 1

Powders of La_2O_3 , SrO and CuO (each having a particle size of less than 10 micron) were mixed with atom ratios of $\text{La}:\text{Sr}:\text{Cu}$ of 1.5 : 0.4 : 1.0. The resulting mixture was then fed to a friction driving type extruder (Conforming unit) shown in Fig. 3 and was extruded at 800 °C to produce a rod. The extruded rod was then heated at 1,100 °C for 2 hours to produce a mass of oxide having the layered perovskite structure by solid reaction.

The resulting mass of oxide of a rod-shape having a diameter of 6 mm had a chemical composition of $\text{La}_{1.5}\text{Sr}_{0.4}\text{O}_{4.0}$ and showed a critical temperature of 38 K when it was measured by usual DC four probe method.

Then, the mass of oxide is inserted in a copper pipe (an outer diameter of 9 mm and an inner diameter of 6.5 mm) as is shown in Fig. 1 in which 1 was a copper pipe and 2 was the mass of oxide.

The composite (1+2) was subjected to swaging work to obtain a wire having an outer diameter of 3 mm.

The resulting wire showed superconductivity and functioned as a superconducting wire. It was also approved that the wire did not melted down even the wire was placed under ordinary conductive condition during electric current is maintained, so that the outer copper layer surrounding the mass of oxide functioned as a stabilizer.

Example 2

Powders of Y_2O_3 , Ba_2CO_3 and CuO were mixed with such atom ratios of $\text{Y}:\text{Ba}:\text{Cu}$ as 1 : 2 : 3 and the resulting mixture was sintered at 900 °C for 12 hours.

The resulting sintered body was pulverized to obtain a sintered powder which was then press-molded into a rod having an outer diameter of 5 mm and a length of 30 cm. The press-molded rod was then sintered at 900 °C for 2 hours to obtain a mass of oxide.

A pipe of Nb having an inner diameter of 5.5 mm was put on the mass of oxide and the resulting composite pipe of outer Nb pipe containing the mass of oxide therein was subjected to swaging operation to reduce its outer diameter to 2 mm.

The resulting wire showed T_c (Critical temperature) of 77 K and J_c (Critical current density) of 200 A.

Then, the outer Nb pipe was removed by etching with nitric acid. The resulting naked mass of oxide was heat-treated at 945 °C for 12 hours and then cooled down to ambient temperature at a rate of 2 °C/min.

The obtained final wire showed T_c of 90 K and J_c of 5,000A at 77K.

Example 3

36.42 % by weight of commercially available Bi_2O_3 powder, 23.07 % by weight of commercially available SrCO_3 23.07 % by weight of commercially available CaCO_3 and 24.87 % by weight of commercially

available CuO were mixed in an attritor in wet and then dried. The dried powder was compacted under a pressure of 1,000 kg/cm² and then sintered at 800 °C in air for 5 hours. The sintered body was pulverized.

The resulting sintered powder was press-molded into a rod having an outer diameter of 6 mm and a length of 50 mm and then sintered at 830 °C for 12 hours.

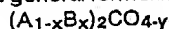
The sintered rod or mass of oxide was covered with a silver pipe having an inner diameter of 6.5 mm and the composite of the silver pipe and the mass of oxide was subjected to swaging operation to obtain a wire having a diameter of 2 mm. The resulting wire showed T_c of 77 K and J_c of 200 A.

The wire was further heat-treated at 830 °C for 12 hours and then quenched. The resulting wire showed T_c of 80 K.

Claims

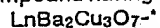
1. A process for manufacturing a wire made of oxide, characterized by steps comprising preparing a mass of oxide having superconductivity from powder material, covering the mass of oxide with a metal pipe, and then reducing the diameter of the metal pipe containing the mass of oxide therein into a wire form by such plastic deformation that exert mainly compressive strain upon the metal pipe.

2. Process claimed in Claim 1, characterized in that said mass of oxide is a compound having the general formula:



in which "A" stands for at least one element selected from lanthanide elements of the Periodic Table, "B" stands for at least one element selected from a group comprising Ia, IIa and IIIa elements of the Periodic Table, "C" stands for at least one element selected from a group comprising Ib, IIb, IIIb elements or transition elements of the Periodic, and small letters "x" and "y" are numbers which satisfy $0 < x < 1$, and $0 \leq y < 4$.

3. Process claimed in Claim 1, characterized in that said mass of oxide is made of a compound having the general formula:



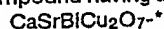
in which "Ln" stands for an element selected from IIIb group elements of the Periodic Table and a symbol of " δ " is a number which satisfies $0 < \delta \leq 1$.

4. Process claimed in Claim 3, characterized in that said Ln is Y.

5. Process claimed in Claim 3, characterized in that said Ln is a lanthanide element.

6. Process claimed in Claim 5, characterized in that said Ln is Ho.

7. Process claimed in Claim 1, characterized in that said mass of oxide is made of a compound having the general formula:



in which a symbol of " δ " is a number which

satisfies $0 < \delta \leq 3$.

8. Process claimed in Claim 1, characterized in that said metal pipe is made of a metal selected from a group comprising Cu, Al, Nb, V, Mo, Ta, and Ag and of an alloy including these metals as the base.

9. Process claimed in Claim 1, characterized in that said mass of oxide is produced by steps comprising extruding a material powder to obtain an molded article and then heat-treating the molded article.

10. Process claimed in Claim 9, characterized in that said heat-treatment is carried out at a temperature ranging from 700 to 1,000 °C.

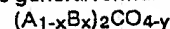
11. Process claimed in Claim 9, characterized in that said extrusion is performed by a friction driving type extruder.

12. Process claimed in Claim 1, characterized in that said plastic deformation is performed by swaging.

13. Process claimed in Claim 1, characterized by further heat-treatment after the plastic deformation.

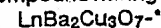
14. A process for manufacturing a wire made of oxide, characterized by steps comprising molding a powder mixture into a rod shape, heating the molded rod to produce a mass of oxide having superconductivity, covering the mass of oxide with a metal pipe, and then reducing the diameter of the metal pipe containing the mass of oxide therein into a wire form by such plastic deformation that exert mainly compressive strain upon the metal pipe.

15. Process claimed in Claim 14, characterized in that said mass of oxide is a compound having the general formula:



in which "A" stands for at least one element selected from lanthanide elements of the Periodic Table, "B" stands for at least one element selected from a group comprising Ia, IIa and IIIa elements of the Periodic Table, "C" stands for at least one element selected from a group comprising Ib, IIb, IIIb elements or transition elements of the Periodic, and small letters "x" and "y" are numbers which satisfy $0 < x < 1$, and $0 \leq y < 4$.

16. Process claimed in Claim 14, characterized in that said mass of oxide is made of a compound having the general formula:



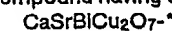
in which "Ln" stands for an element selected from IIIb group elements of the Periodic Table and a symbol of " δ " is a number which satisfies $0 < \delta \leq 3$.

17. Process claimed in Claim 16, characterized in that said Ln is Y.

18. Process claimed in Claim 16, characterized in that said Ln is a lanthanide element.

19. Process claimed in Claim 18, characterized in that said Ln is Ho.

20. Process claimed in Claim 14, characterized in that said mass of oxide is made of a compound having the general formula:



in which a symbol of " * " is a number which satisfies $0 < * \leq 3$.

21. Process claimed in Claim 14, characterized in that said metal pipe is made of a metal selected from a group comprising Cu, Al, Nb, V, Mo, Ta, and Ag and of an alloy including these metals as the base.

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22. Process claimed in Claim 14, characterized in that said molding is performed by extrusion.

23. Process claimed in Claim 22, characterized in that said extrusion is performed by a friction driving type extruder.

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24. Process claimed in Claim 14, characterized in that the molded article is heated at a temperature ranging from 700 to 1,000 °C.

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25. Process claimed in Claim 14, characterized in that said plastic deformation is performed by swaging.

26. Process claimed in Claim 14, characterized by further heat-treatment after the plastic deformation.

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FIGURE 1

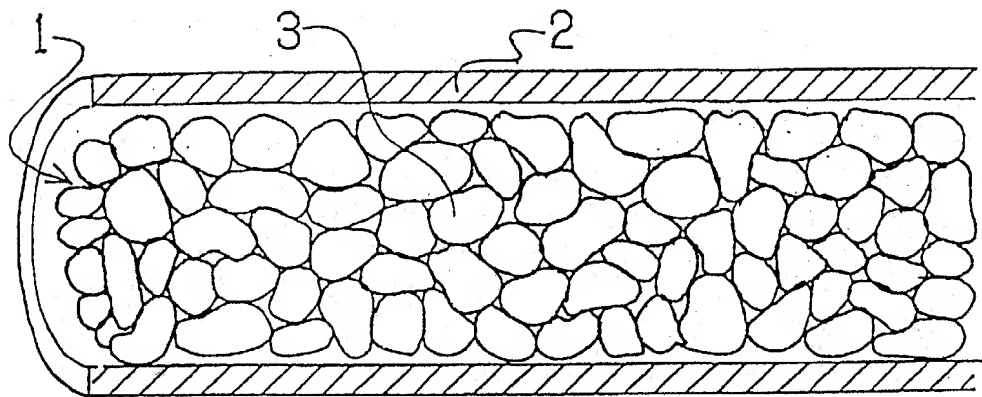
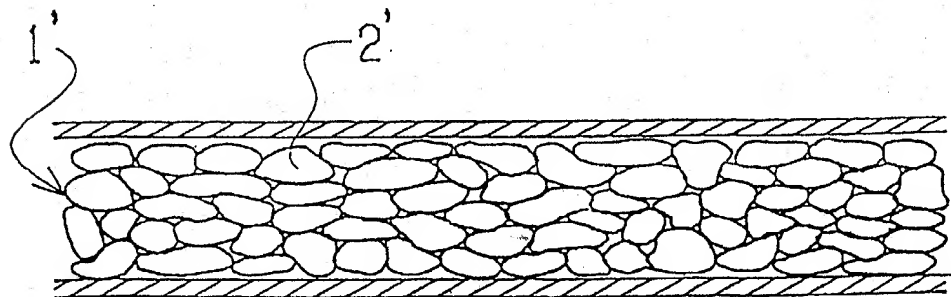


FIGURE 2



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FIGURE 3

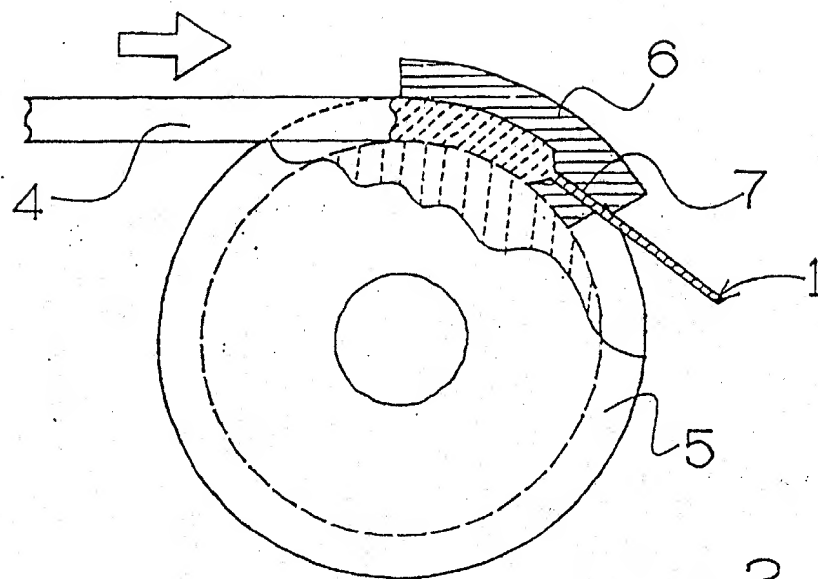


FIGURE 4

